PATENT

44006

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of	
Eduardo TERRES ROJAS et al.	Art Unit: 1755
Serial No.: 10/620,770	Examiner David R. Sample
Filed: July 17, 2003	
For: SYNTHETIC MESOPOROUS MATERIAL WITH RADIALLY ASSEMBLED NANOTUBES	

DECLARATION UNDER 37 C.F.R. § 1.132

Jose Manuel Dominguez Esquivel declares as follows:

1. I hold a PhD degree from Claude Bernard University, at Lyon, France. I am currently employed by Instituto Mexicano Petroleo as Research Executive. I have been working in the field of catalysis and materials science for 25 years.

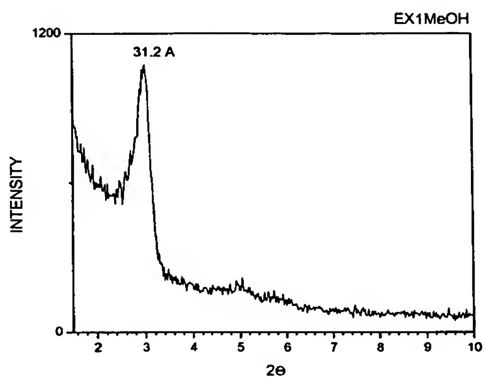
2. I am co-inventor of the subject matter described and claimed in the above-identified application.

3. I have reviewed the Official Action dated March 24, 2005 and U.S. Patent No. 6,096,469 to Anderson et al ("Anderson et al patent").

4. Under my supervision and direction, tests were conducted to reproduce Examples 1 and 2 of the Anderson et al patent referred to on page 2 of the aforesaid Office Action, and to test the products obtained to determine their nature. The procedures stated in Examples 1 and 2 were followed as described in Exhibits 1a and 1b attached hereto (Synthesis diagrams).

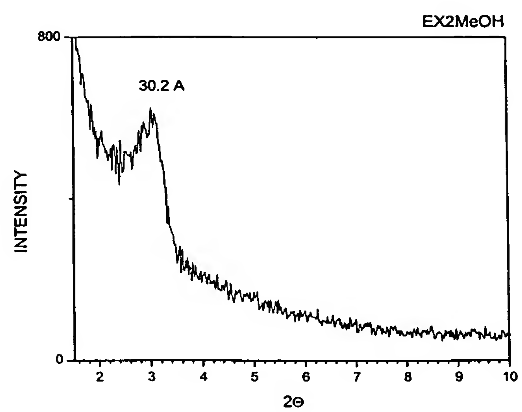
5. The product formed in the procedure corresponding to the Anderson et al Example 1 using as precursors, methanol (MeOH), tetramethoxysilane (TMOS) and

tetradecyltrimethylammonium bromide ($C_{14}TAB$) was tested using x-ray diffraction, nitrogen adsorption and transmission electron microscopy. A sample of the product of was tested and revealed a BET surface area of 1065 m^2/g, a total pore volume of 0.698 cc/g and an average pore diameter of 2.6 nm. An x-ray diffraction pattern of the sample is shown below and reveals a main peak at d = 3.12 nm and shows a certain degree of pore ordering for this sample.



6. The results of the electron microscopy analysis of the product of the Anderson et al Example 1 is shown in attached Exhibits 2-7. Exhibit 2 is a general overview showing the typical particle aggregates, where most of the particles (> 95%) are irregularly shaped or ellipsoidal, with sizes between about 0.3 to 1 μm. Exhibit 3 shows different particles, one of them is almost spherical. Exhibit 4 shows the inner structure of a typical ellipsoidal particle. Exhibit 5 shows typical faceted particle with a well ordered pores array (hexagonal symmetry). Exhibit 6 shows three particles with different shapes and structures. The rounded particle has an "amorphous-like" inner structure; the particle at the right-hand side shows a jagged fracture surface; the upper particle is layered. Exhibit 7 shows a region with "necked particles" which have a rounded shape and "amorphous"-like inner structure (random distribution of pores).

7. The product formed in the procedure corresponding to the Anderson et al Example 2 also using as precursors, methanol (MeOH), tetramethoxysilane (TMOS) and tetradecyltrimethylammonium bromide ($C_{14}TAB$) was tested using x-ray diffraction, nitrogen adsorption and transmission electron microscopy. A sample of the product of was tested and revealed a BET surface area of 1198 m^2/g, a total pore volume of 0.664 cc/g and an average pore diameter of 22 A. An x-ray diffraction pattern of the sample is shown below and reveals a main peak at d = 3.12 nm and indicates a deep structural relaxation leading to a poor pore ordering with respect to that of the Example 1 sample.



8. The results of the electron microscopy analysis of the product of the Anderson et al Example 2 is shown in attached Exhibits 8-13. Exhibit 8 is a general overview showing the typical (thick) aggregates with most of the particles (> 99%) having irregular shapes or ellipsoidal outlines (pear-shaped), with sizes between about 0.3 to 1 μm. Exhibit 9 is a magnified view of another area of the same sample. Exhibit 10 is a magnified view of still another area of the same sample. Exhibit 11 shows a typical pear-shaped particle. In this case the inner structure consists of parallel twisted planes. Exhibit 12 shows another pear-shaped particle with a well ordered pore system (i.e., hexagonal symmetry). Exhibit 13 shows the

inner structure of a typical irregular particle belonging to the same sample in which only some pore arrays are apparent.

9. The foregoing micrographs of samples from Examples 1 and 2 from the Anderson et al patent verify the formation of silica particles, which have a variety of shapes and sizes, i.e., ellipsoidal, pear-shaped, faceted, rounded-irregular and jagged fractured surfaces, with sizes between 0.3 and 1 μm. The inner structure of some particles consisted of incipient arrays of pores, some having one-dimensional channels, but, in general, those particles presented a random distribution of pores or amorphous-like texture. Their porosity was high, i.e., surface areas between 1065 and 1198 m^2/g and a mean pore size between 2.6 and 3.6 nm.

In short, the product of Anderson et al, as indicated in Examples 1 and 2 are silica particles having a great diversity of shapes and their inner pore structure is either one-dimensional or distributed at random (amorphous-like). Unlike the silica particles described in our application, testing of the Anderson et al spherical silica particles reveal that they do not have an inner structure formed by chain stacks aligned along the radius of the spherical particle where each of the chain stacks have pores interconnected with pores of an adjacent chain stack to define a nanotube structure. Testing of the Anderson et al elliptical particles reveal that such particles do not have an inner structure formed by chain stacks oriented substantially parallel to the major axis of the particle with pores interconnected with pores of an adjacent chain stack to define a plurality of nanotubes. Elliptical particles formed by Anderson contained pores aligned perpendicular to a major axis.

10. By comparison, our above-captioned patent application describes the production of spherical and elliptical silica particles having a diameter between 0.1 and 1 micron having an inner structure formed by chain stacks aligned along the radius and having

pores interconnected with pores of adjacent chain stacks to form a nanotube structure in which the spherical particles have pores extending radially outwardly along the radius of the sphere, and the elliptical particles have pores running parallel to the major axis of the particle.

11. As seen in Exhibits 14 and 15, which correspond to Figures 2 and 3 of our application, as well as Exhibit 16, the spherical silica particles of our invention have an inner structure formed by chain stacks aligned along the radius and having pores interconnected with pores of adjacent chain stacks to form a nanotube structure and have pores extending radially outward along the radius of the sphere from a center of the silica particle. Such particles are produced by using amounts of surfactant, cosolvent and a hydrolysis catalyst effective to produce particles having such inner nanotube structure. The production of spherical particles having the inner structure depicted in Figures 2 and 3 of our application, as well as Exhibits 14-16 attached hereto, is shown by the tests described in our application in Examples 1-9 corresponding to paragraphs 0065-0086 of our application, which tests are incorporated by reference into this declaration. Thus, in such tests an aqueous solution was formed from an organic cosolvent, which ethanol or propanol, a surfactant (CTAB), an ammonium hydroxide catalyst and a silica source, namely tetraethylorthosilicate (TEOS) in effective amounts to form a gel, which is dried and calcined to provide spherical particles having the inner structure of shown in Fig. 2 of our application and verified by XRD and TEM techniques, as described.

12. Similarly, the tests described in Examples 10-17 in paragraphs 0087-0106 produce elliptical particles having an inner structure with 1-D channels running along the longer or major axis of the particle. Thus, in the tests of Examples 10-17, which tests are incorporated by reference into this declaration, an aqueous solution was formed from an organic cosolvent, which is methanol or acetone, a surfactant(CTAB), an ammonium

hydroxide catalyst and a silica source, namely tetraethylorthosilicate (TEOS) in effective amounts to form a gel, which is dried and calcined to form particles having an elliptical shape and an inner structure formed by chain stacks, each of the chain stacks having pores interconnected with pores of an adjacent chain stack to define a plurality of nanotubes verified by XRD and TEM techniques.

13. Effective amounts of cosolvent, surfactant, etc., is discussed in paragraphs 0051-0064 or our application in regard to Table 1 in paragraph 0053. Table 1 is based on 48 silica particles whose inner structural features were verified by x-ray diffraction peak profiles and high resolution transmission electron microscopy (TEM). Fig. 1A of our application shows the peak profiles obtained when ethanol and propanol are used as cosolvent, while Fig. 1B shows the peak profiles when methanol is used as cosolvent. Referring to Table 1, spherical particles having an inner structure formed by chain stacks with radial pores are obtained, for example, using ethanol at S(4,6) and S(4,8) or propanol at S(4,2), S(4,4), S(4,6) and S(4,8), while elliptical particles having an inner structure formed by chain stacks having pores running parallel to a major axis and interconnected with pores of an adjacent chain stack are formed at with a methanol co-solvent at S(4,6) and S(4,8).

14. The foregoing tests in which Examples 1 and 2 of the Anderson et al patent were reproduced demonstrate that the spherical silica particles tested do not have an inner structure of chain stacks aligned along the radius and forming a nanotube structure with pores extending in a substantially radial direction with respect to the center of the particle with interconnecting pores between adjacent chain stacks, nor do the elliptical silica particles tested have an inner structure formed by chain stacks in which the nanotubes are oriented substantially parallel to the major axis of the particle. Thus, the spherical and elliptical

particles disclosed and claimed in our application are not formed in Examples 1 and 2 of the Anderson et al patent and are not inherently formed.

15. Further demonstrating the lack of inherent formation of spherical and elliptical particles having an inner structure produced in the Examples of our application, the procedures of Examples 1 and 2 of the Anderson et al patent were repeated substituting a different silica source, namely, tetraethoxysilane (TEOS) for tetramethoxysilane (TMOS); an ethanol cosolvent for methanol; and surfactant: hexadecyltrimethylammonium Bromide (C_{16}TAB) surfactant for tetradecyltrimethylammonium bromide (C_{14}TAB). The rest of the reactants and procedures were maintained as stated in Examples 1 and 2, respectively, of the Anderson et al patent, and as depicted in Exhibits 1a and 1b. The resulting particles corresponding to Example 1 are shown in attached Exhibits 17-22, in which Exhibit 17 is a general overview showing the typical particle aggregates, where most of the particles (> 95%) are irregularly shaped, ellipsoidal or have a rectangular outline, with sizes between about 0.2 to 1 μml; Exhibit 18 shows aggregates of irregularly shaped particles; Exhibit 19 shows a typical region showing particles with a rounded shape; Exhibit 20 shows a typical rectangular particle with rounded corners; Exhibit 21 shows a typical twinned rectangular particle of about 100 nm width and 500 nm length; and Exhibit 22 shows a typical spherical particle of about 500 nm diameter having an inner structure that is amorphous.

The resulting particles corresponding to Example 2 are shown in attached Exhibits 23-28, in which attached Exhibit 23, is a general overview showing the aggregation of particles which present an irregular outline; Exhibit 24, is a general overview showing particles having both irregular and rounded shapes; Exhibit 25, is a region of particles with rounded shapes; Exhibit 26, is a typical rounded shaped particle; Exhibit 27, is another typical particle with round shape attached to a bigger aggregate; and Exhibit 28, which shows another region

containing particles with rounded shape. The test results reveal that by following the procedure of Anderson et al, but substituting the materials indicated, there appears to be a slight increase of the proportion of rounded particle shapes. However, the spherical particles obtained did not have an inner structure of chain stacks aligned along the radius of the spherical particle forming a nanotube structure with pores extending in a substantially radial direction with respect to the center of the particle with interconnecting pores between adjacent chain stacks, nor were elliptical silica particles formed having an inner structure formed by chain stacks in which the nanotubes are oriented substantially parallel to the major axis of the particle.

16. The undersigned declares further that all statements made of his own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Dated: August 22, 2005

Jose Manuel Dominguez Esquivel

SYNTHESIS OF STS (U.S. 6,096,469)

STS: SURFACTANT TEMPLATED SILICA PARTICLES

Example 1

4 L Glass Jar: 40 g C_{14}TAB + 490 g MeOH + 980 g H2O + 490 g NH4OH

↓

Stir until C14TAB dissolution

↓

Add 128 g TMOS

↓

Final Molar weight ratio: 1 TMOS:0.13 C_{14}TAB: 56 H_2O:18 MeOH: 4.6 NH_4OH

↓

Shake "by hand" (≈ 30 s)

↓

The gel stands "overnight"

↓

Filtering + Washing (H2O)

↓

Drying "overnight", 100 °C, air.

↓

Calcining at 550 °C, in N_2-1.5 h, + calcining in air at 550 °C-6 h

↓

Deaggregation of the particles : 47.8 g of Powdered STS was added to 159 ml H_2O, then it was ground in 1 L Ball Mill (2.5 h)

Final Result: **Result**: 250-400 nm Spherical and Ellipsoidal particles with a small fraction of < 50 nm primary particles

EXHIBIT 1a

2

SYNTHESIS OF STS (U.S. 6,096,469)

STS: SURFACTANT TEMPLATED SILICA PARTICLES

Example 2

40 g C_{14}TAB + 490 g MeOH +
980 g H2O + 490 g NH4OH

↓

Add 128 g TMOS from a separation funnel
(in about 2.5 min)

↓

Stir with a high shear mixer for 5 min, with
increasing shear rate from 500 to 14000 rpm

↓

The gel stands "overnight"

↓

Filtering + Washing (H2O)

↓

Drying "overnight", 100 °C, air.

↓

Calcining at 550 °C, in air, 6 h

↓

Formation of slurry:
20 g of Powdered STS was
added to 46.7 ml H_2O, then it was shear mixed
at 1000 rpm, 2 min, then it was turned into paste

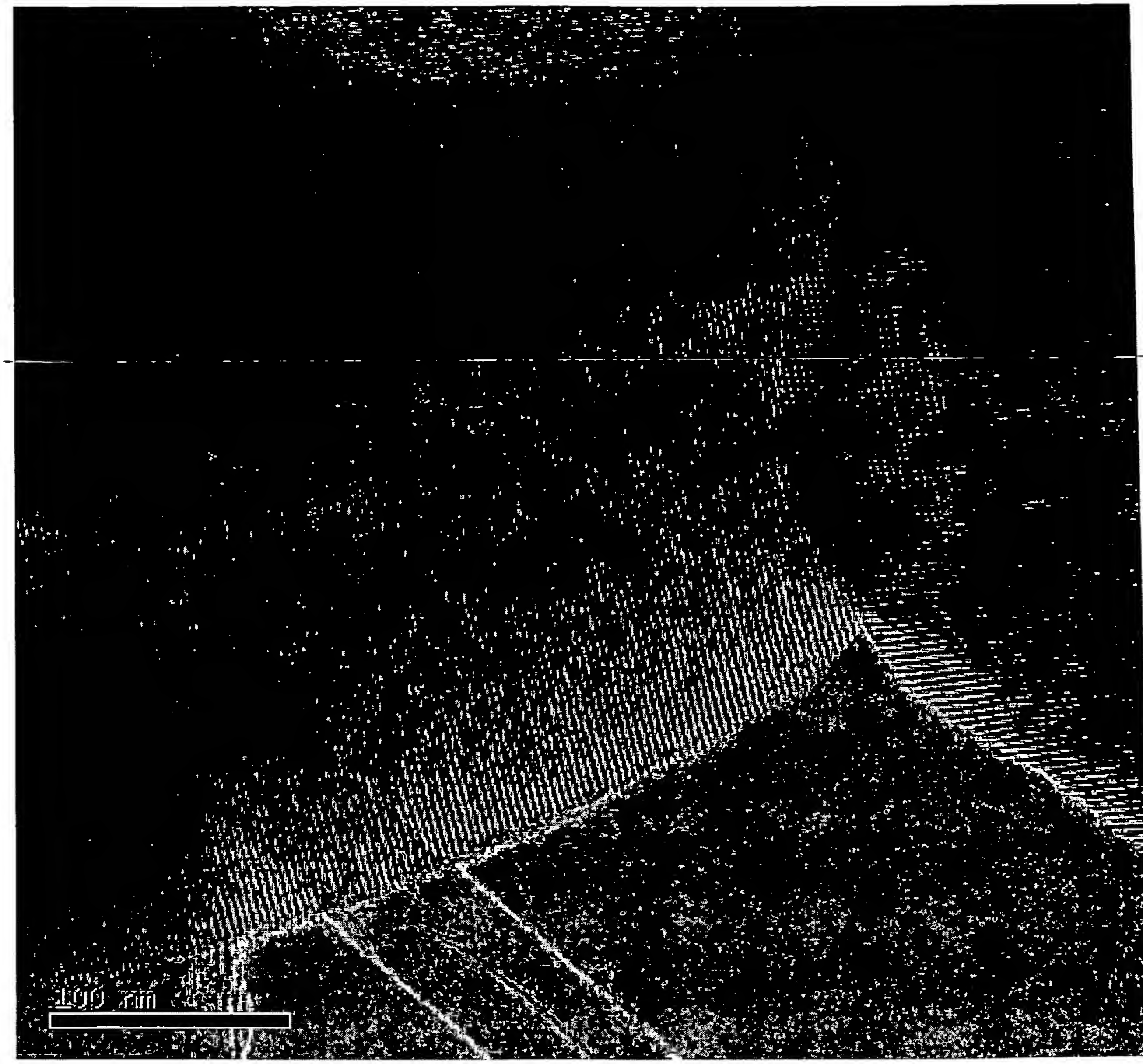
↓

Result: 250-500 nm spherical and Ellipsoidal
primary particles with a small fraction of < 50 nm
primary particles. Jagged fracture surfaces were
evident on some particles.
XRD indicated 1 peak at 3.46 nm in uncalcined sample.

EXHIBIT 1b

EXHIBIT 2

EXHIBIT 3



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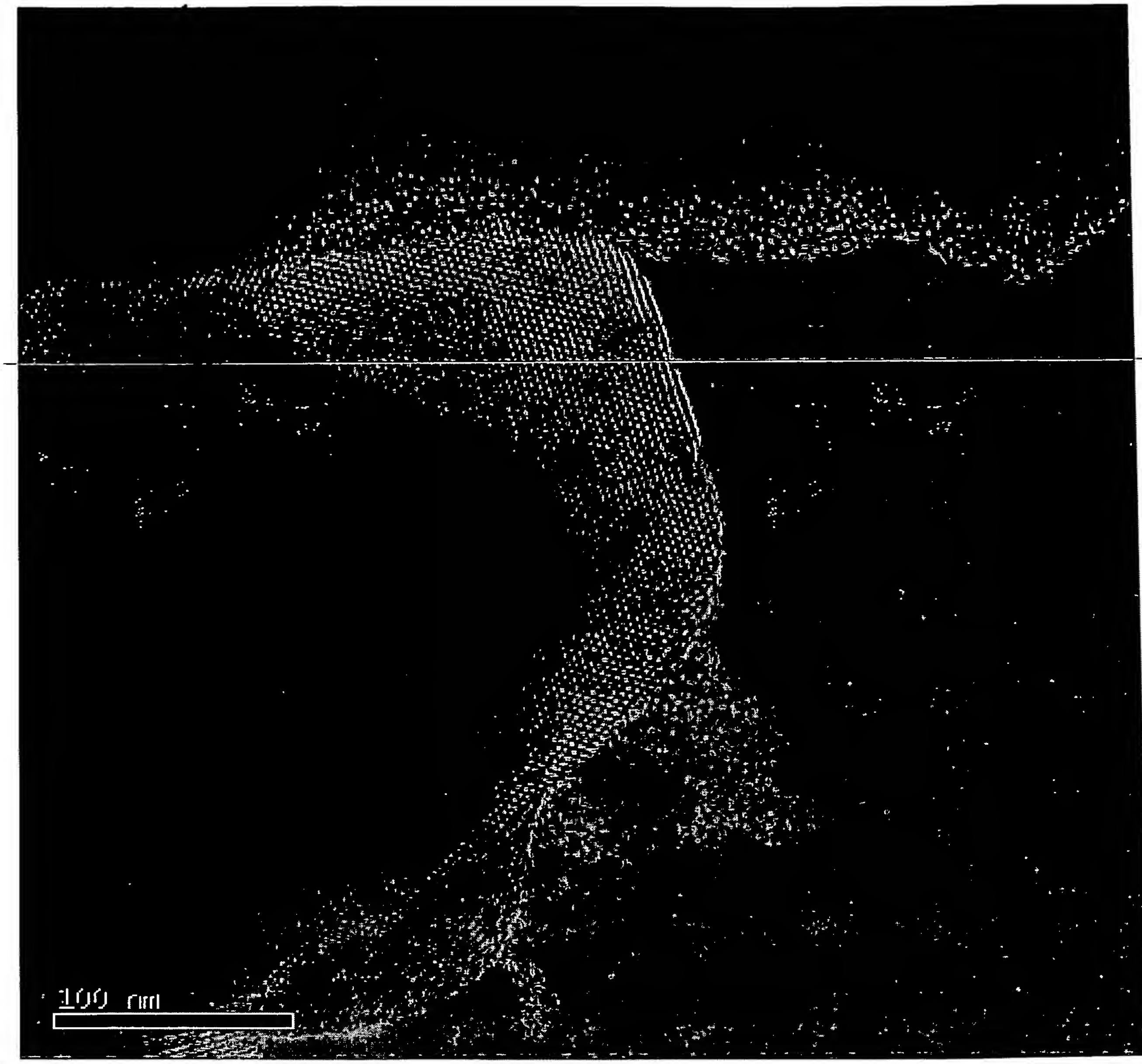

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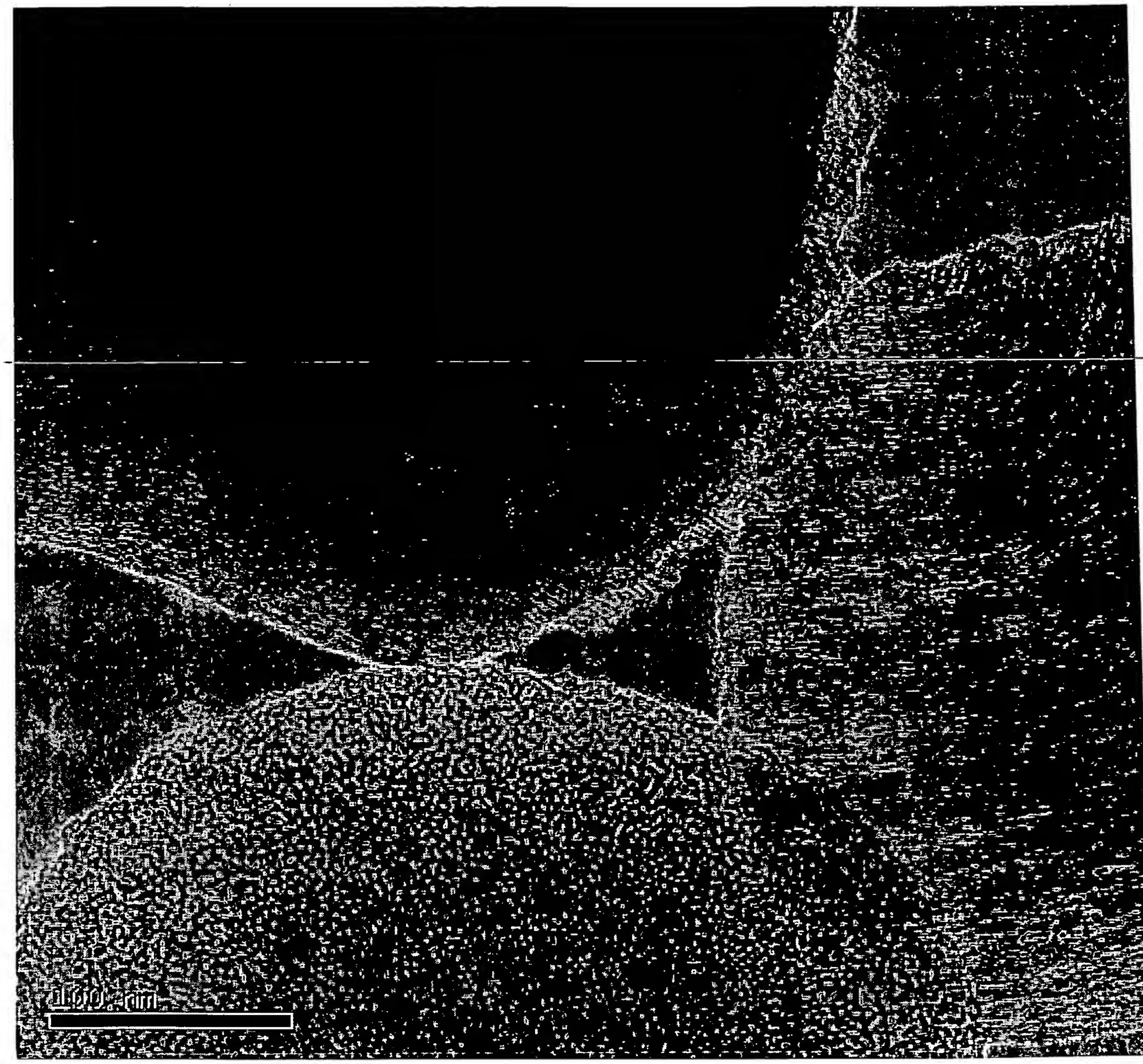


EXHIBIT 6

EXHIBIT 7

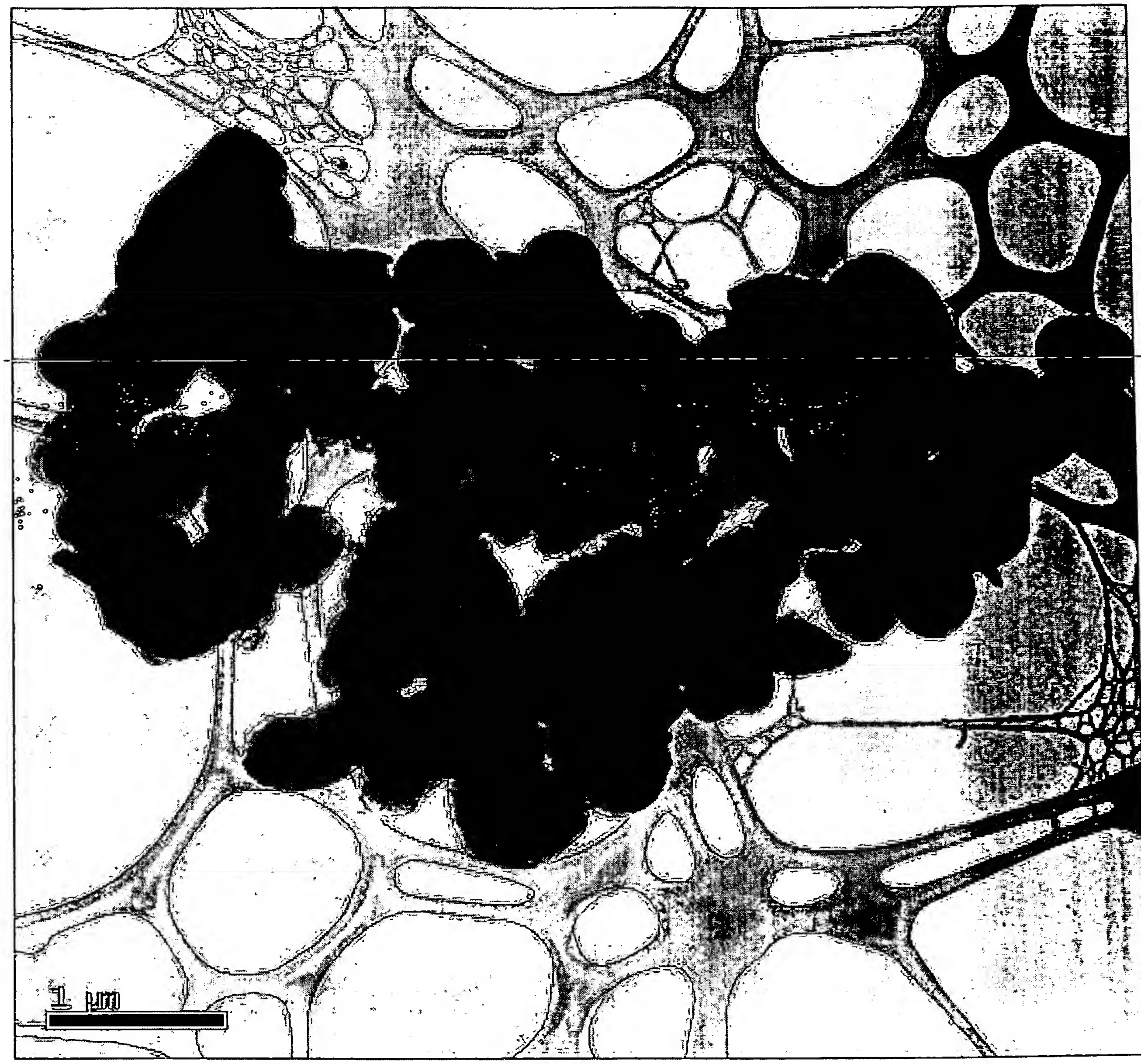


EXHIBIT 8

EXHIBIT 9

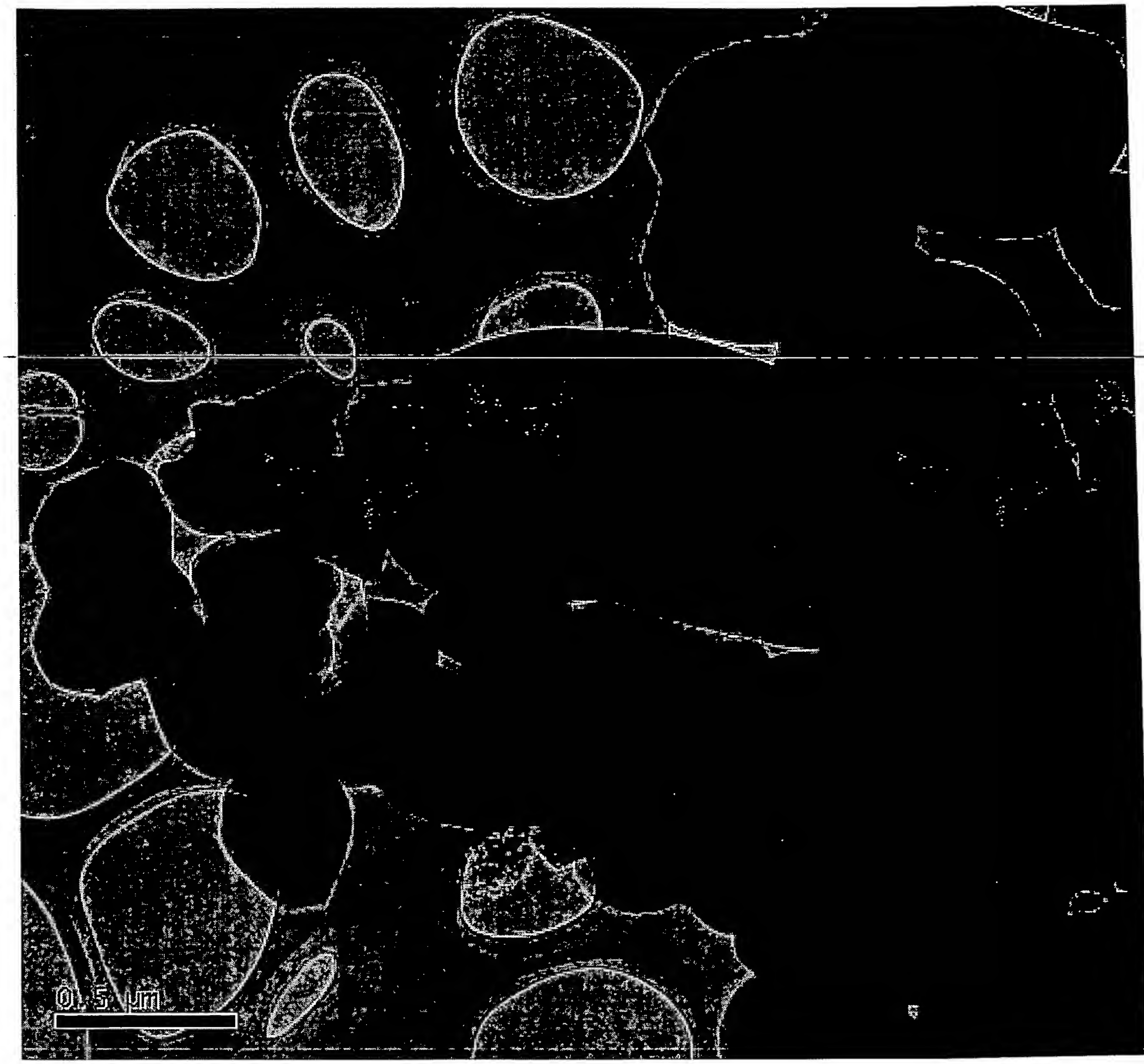
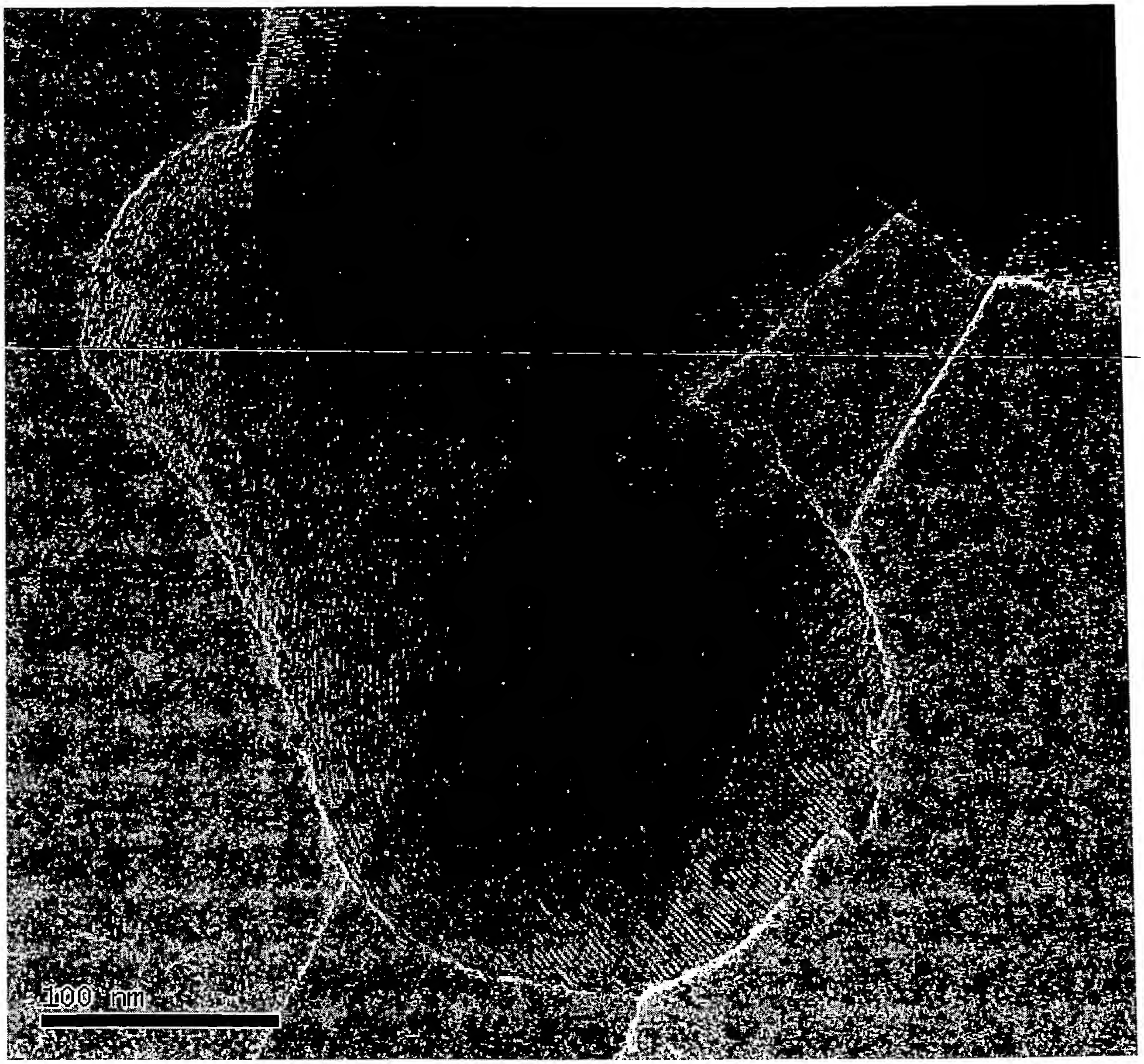


EXHIBIT 10



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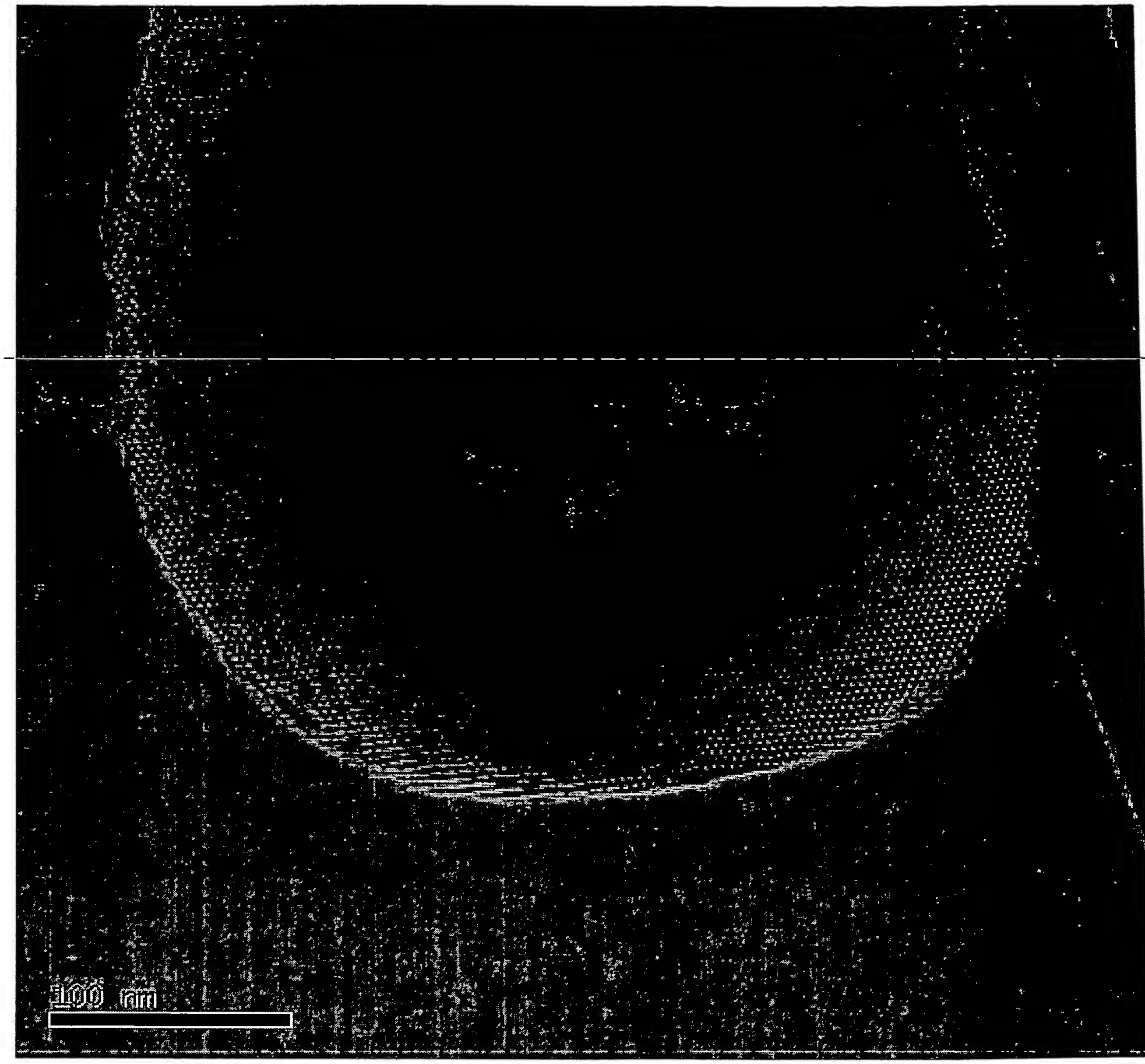

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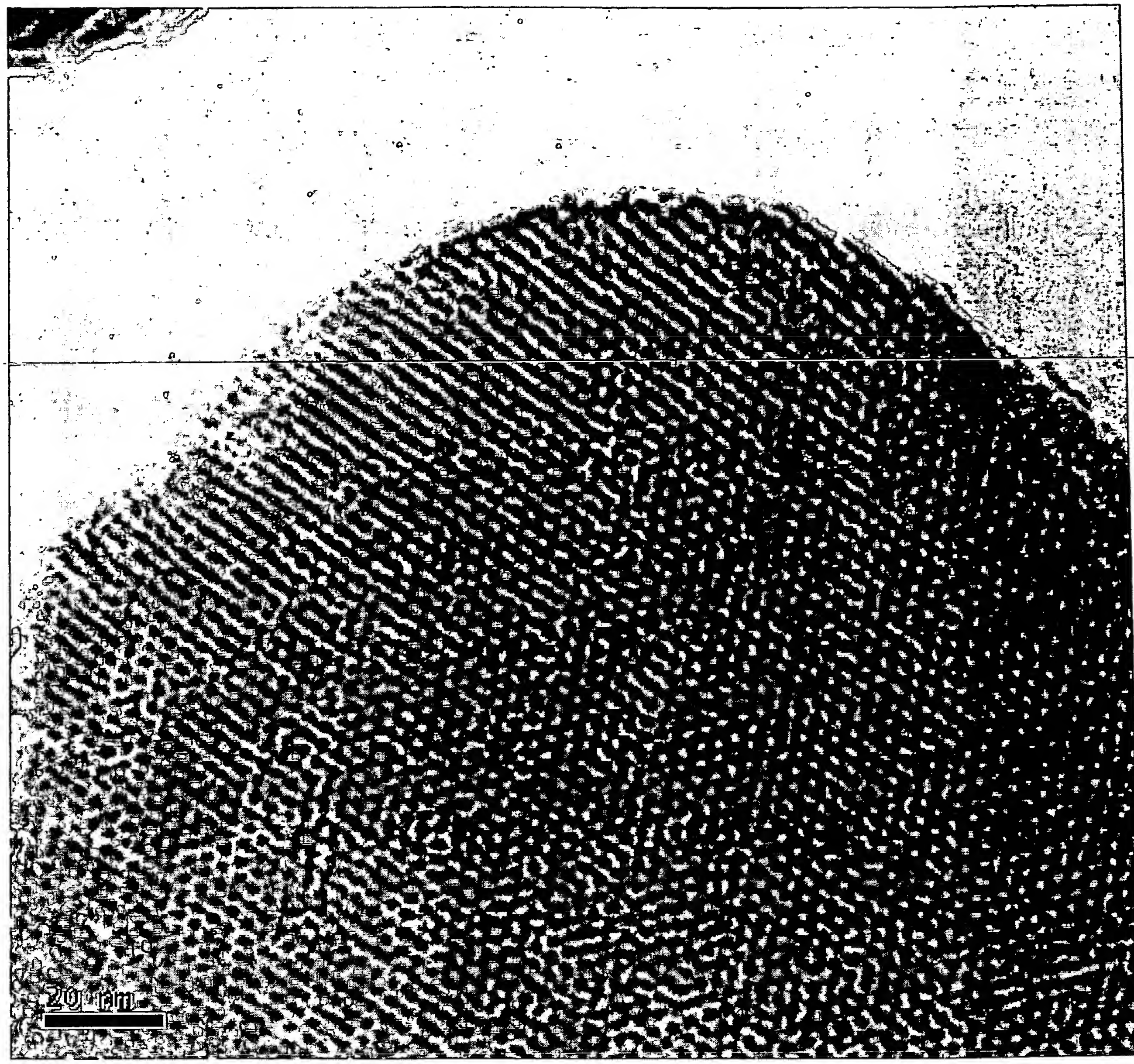

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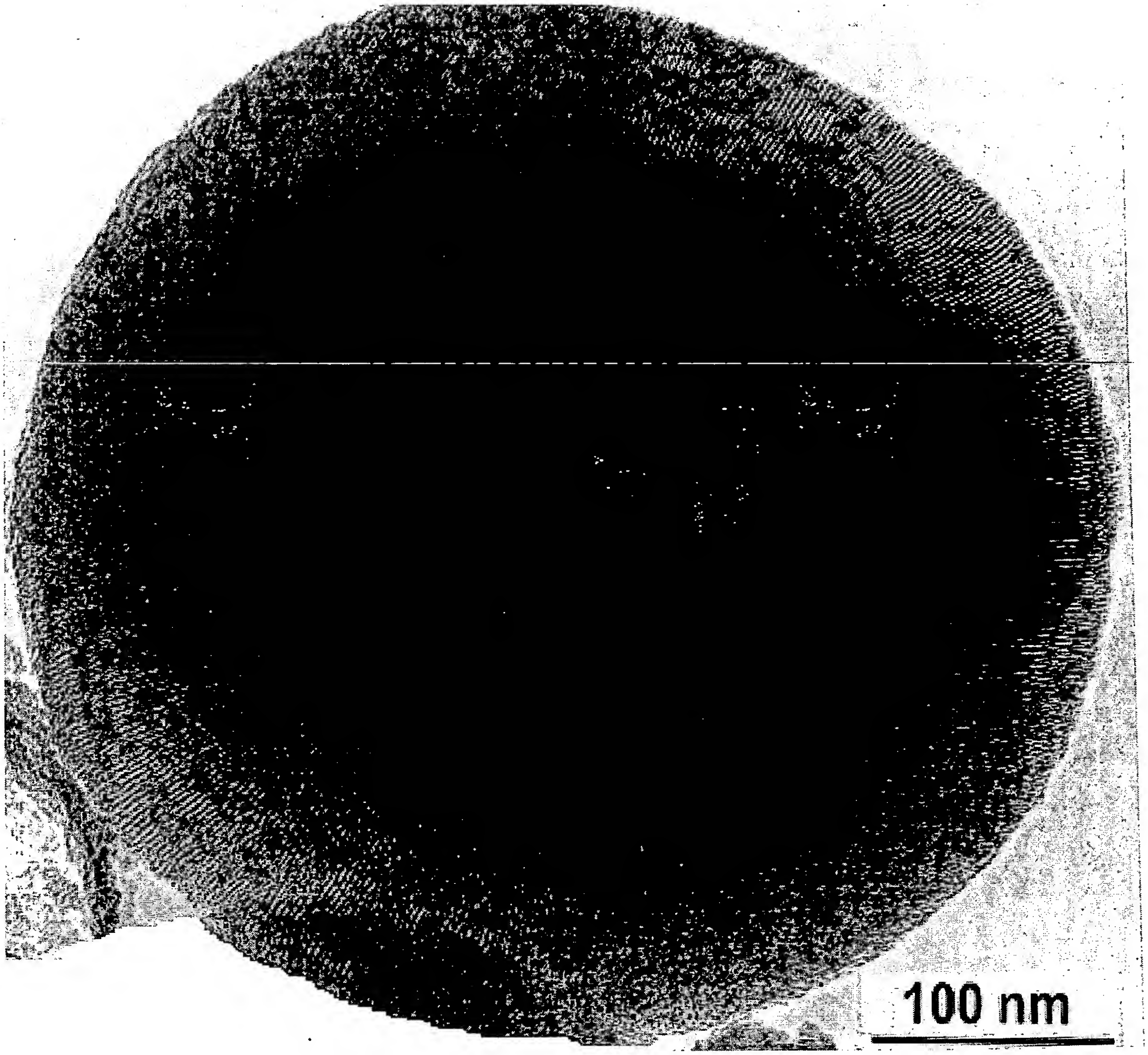
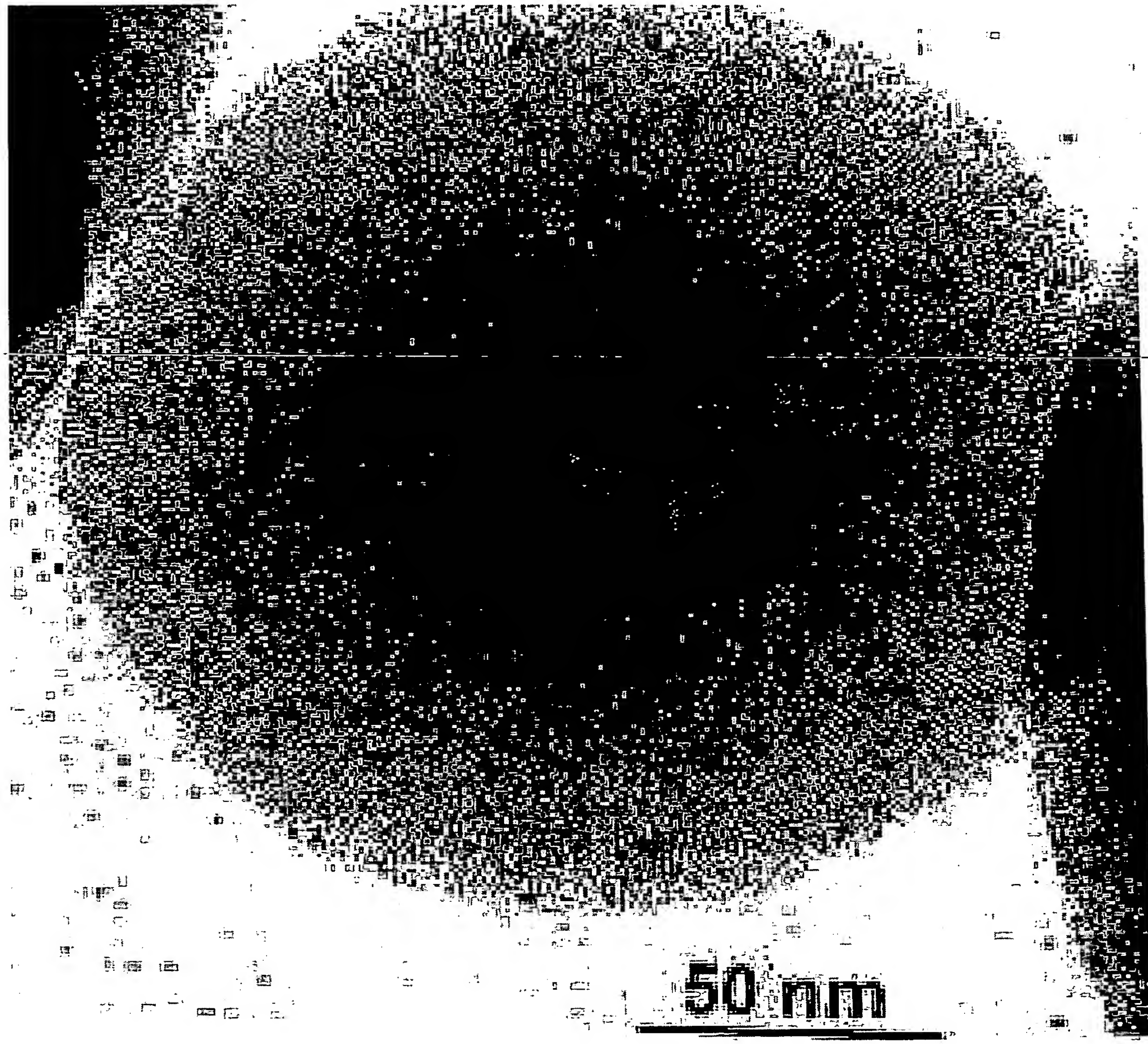


EXHIBIT 14



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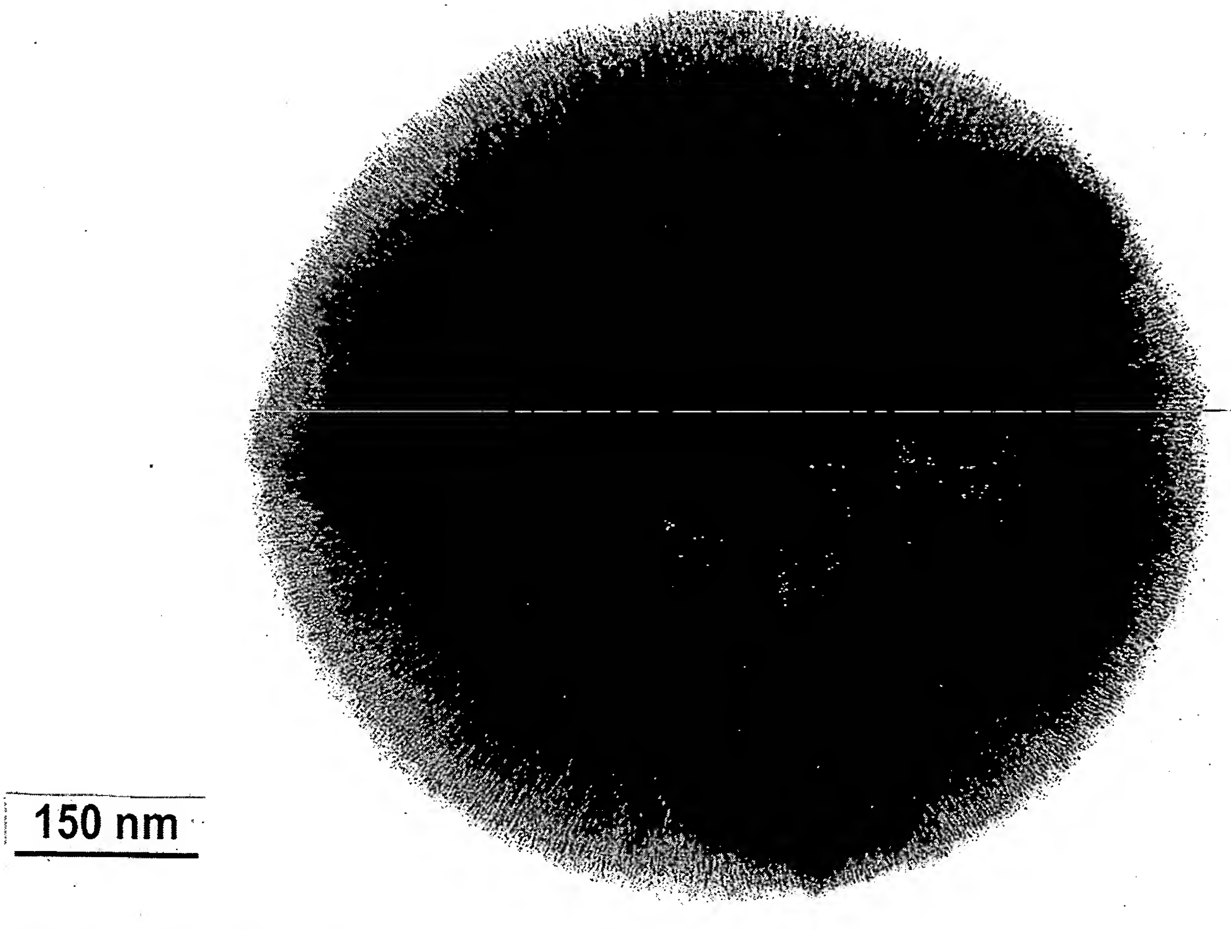

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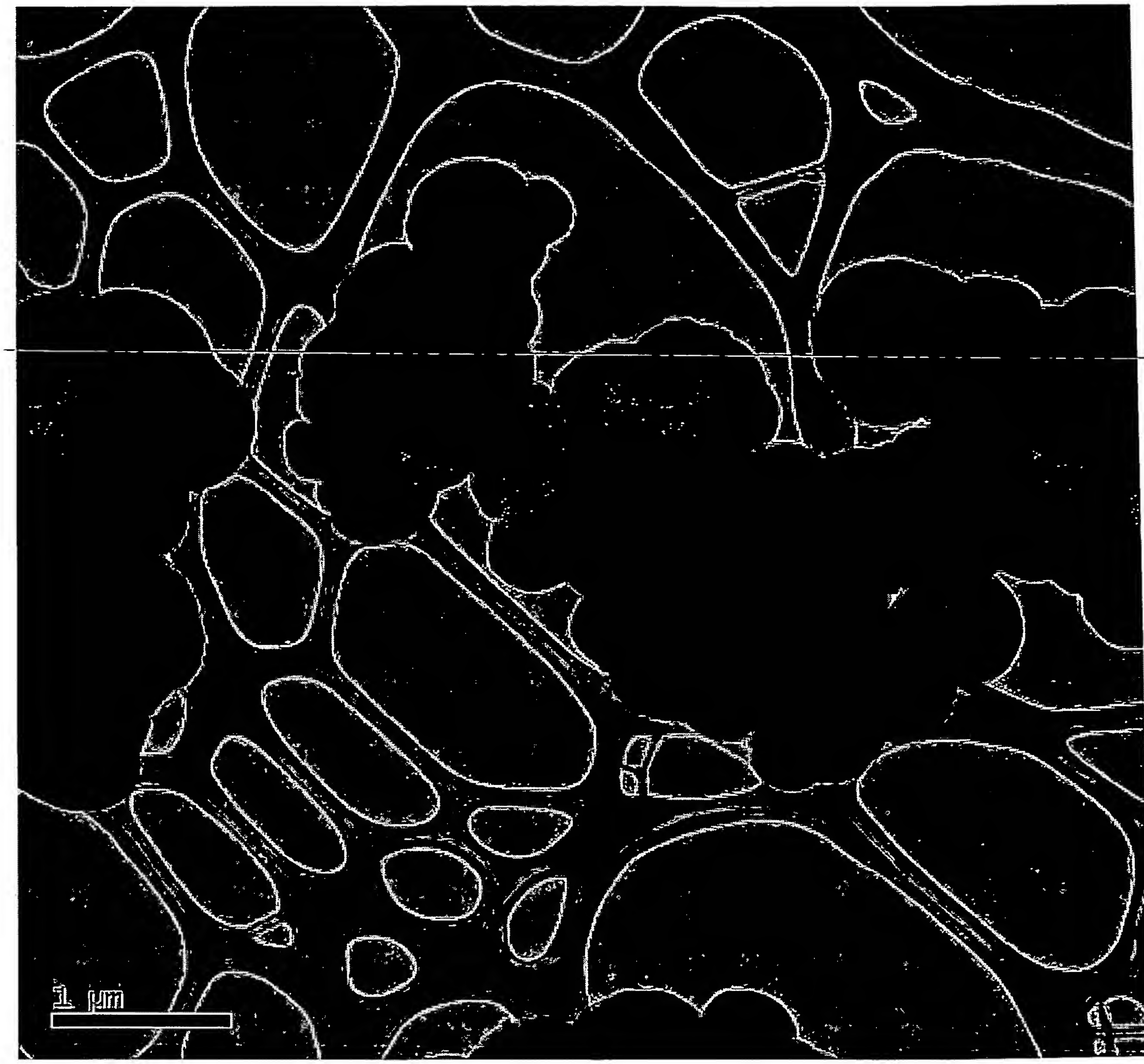
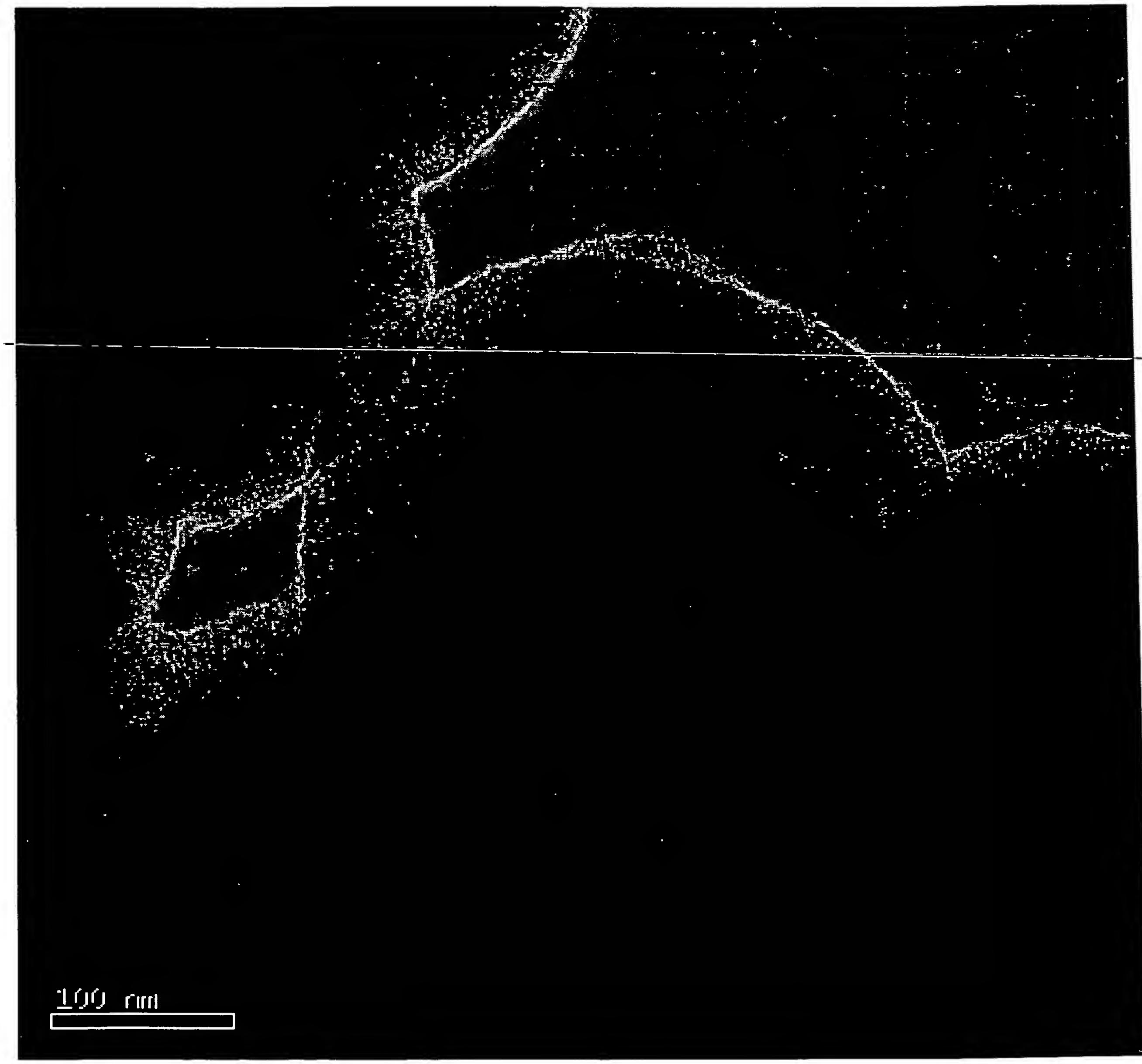


EXHIBIT 17

EXHIBIT 18



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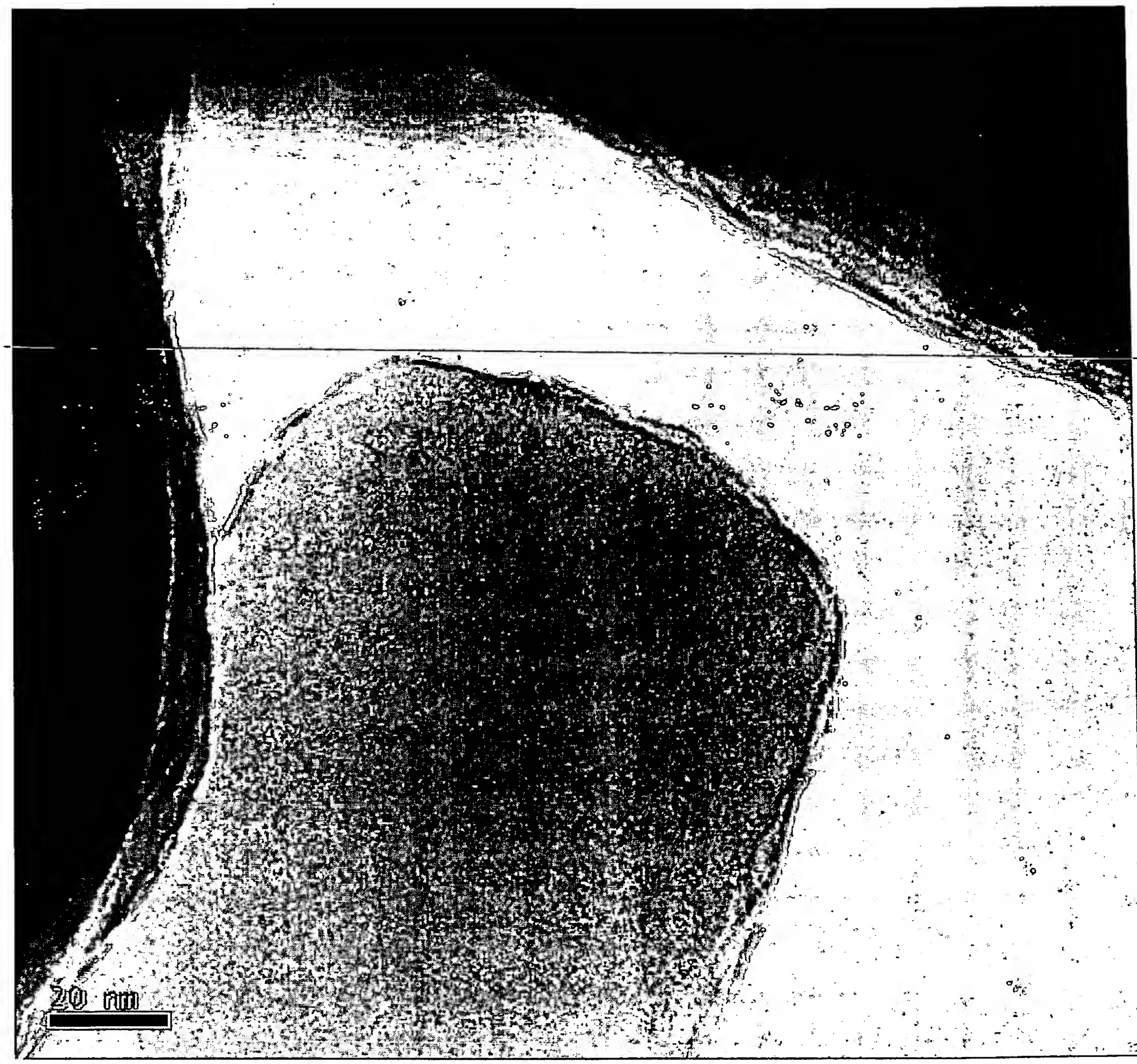


EXHIBIT 20

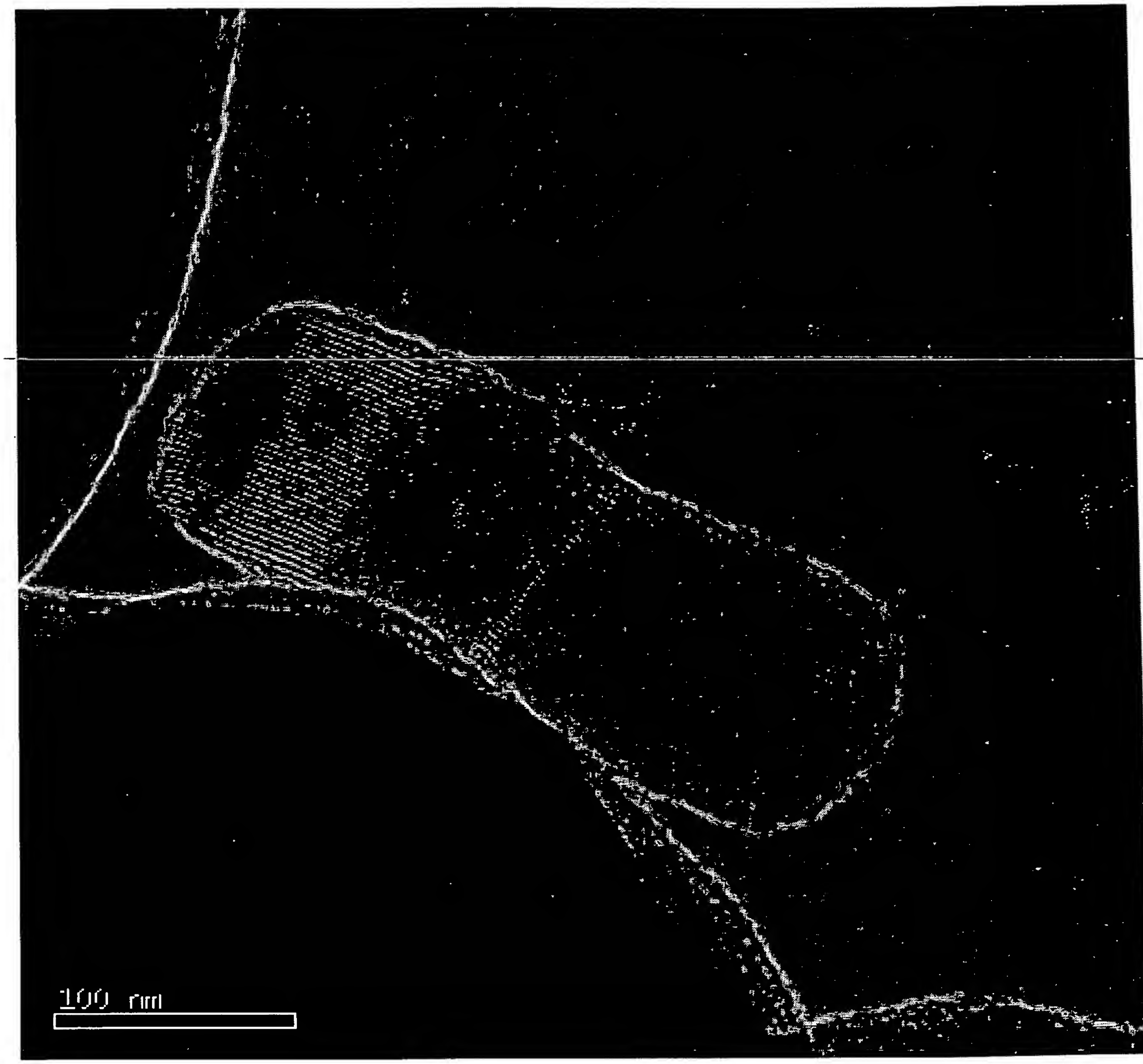


EXHIBIT 21

EXHIBIT 22

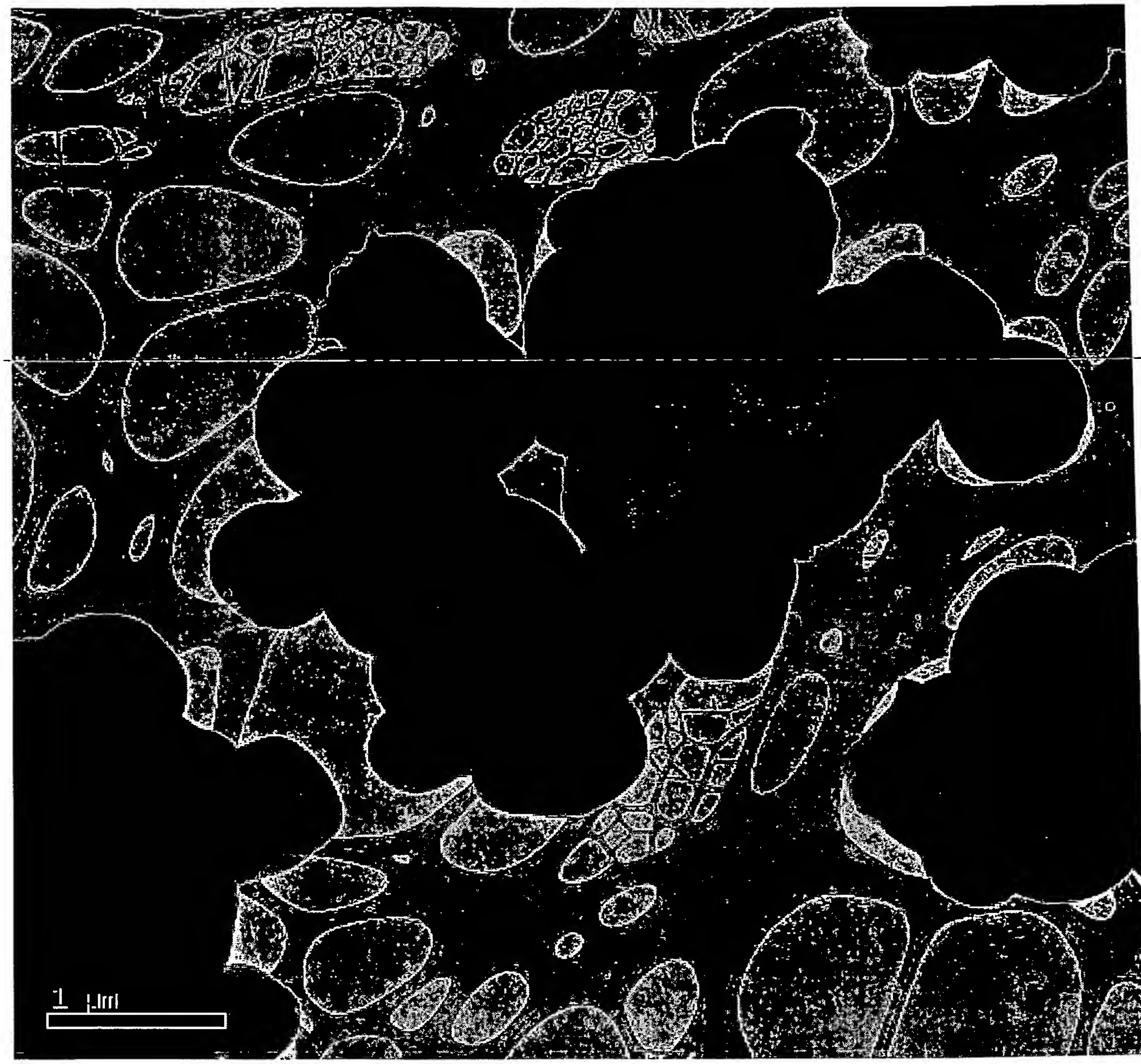
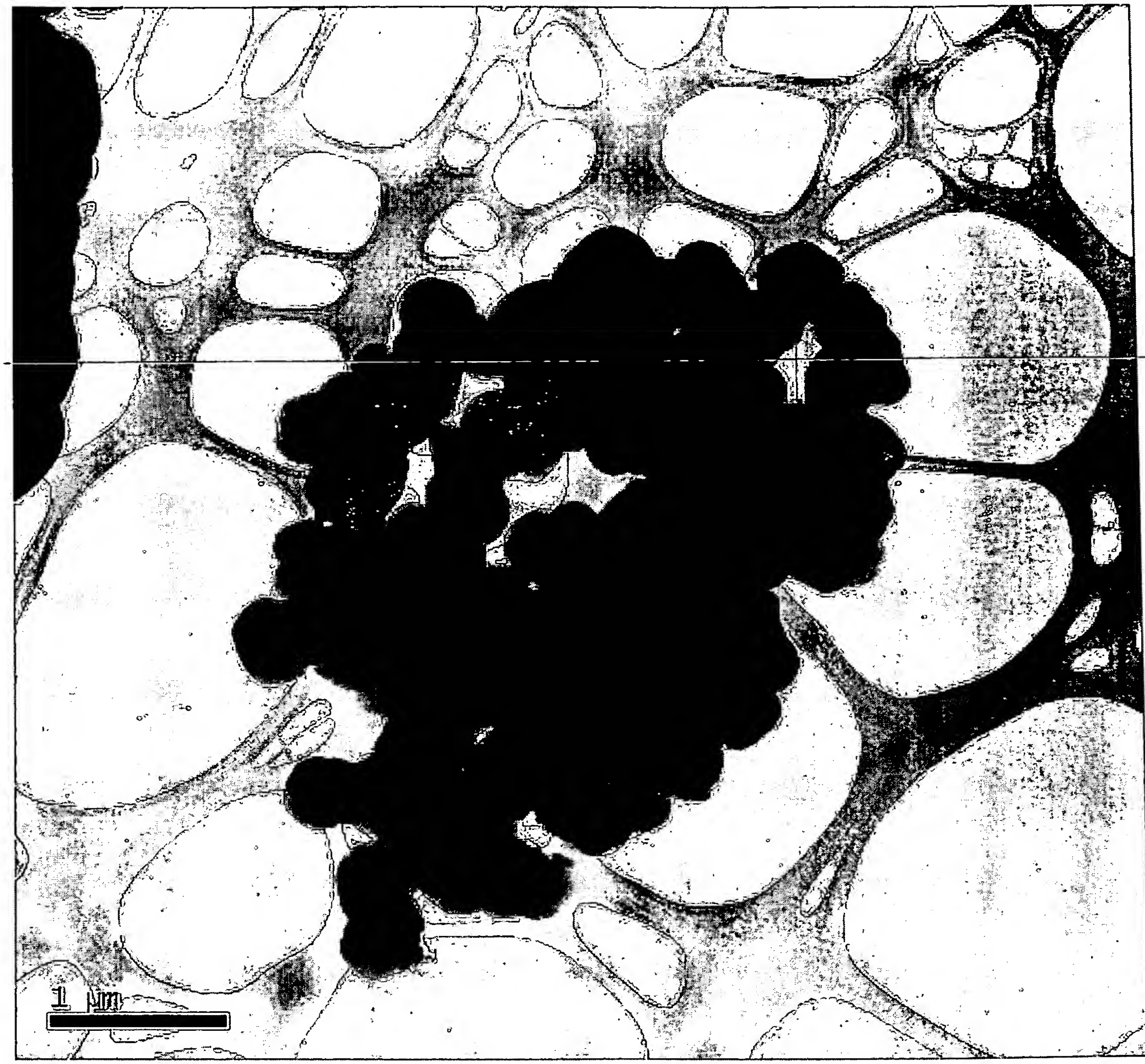


EXHIBIT 23



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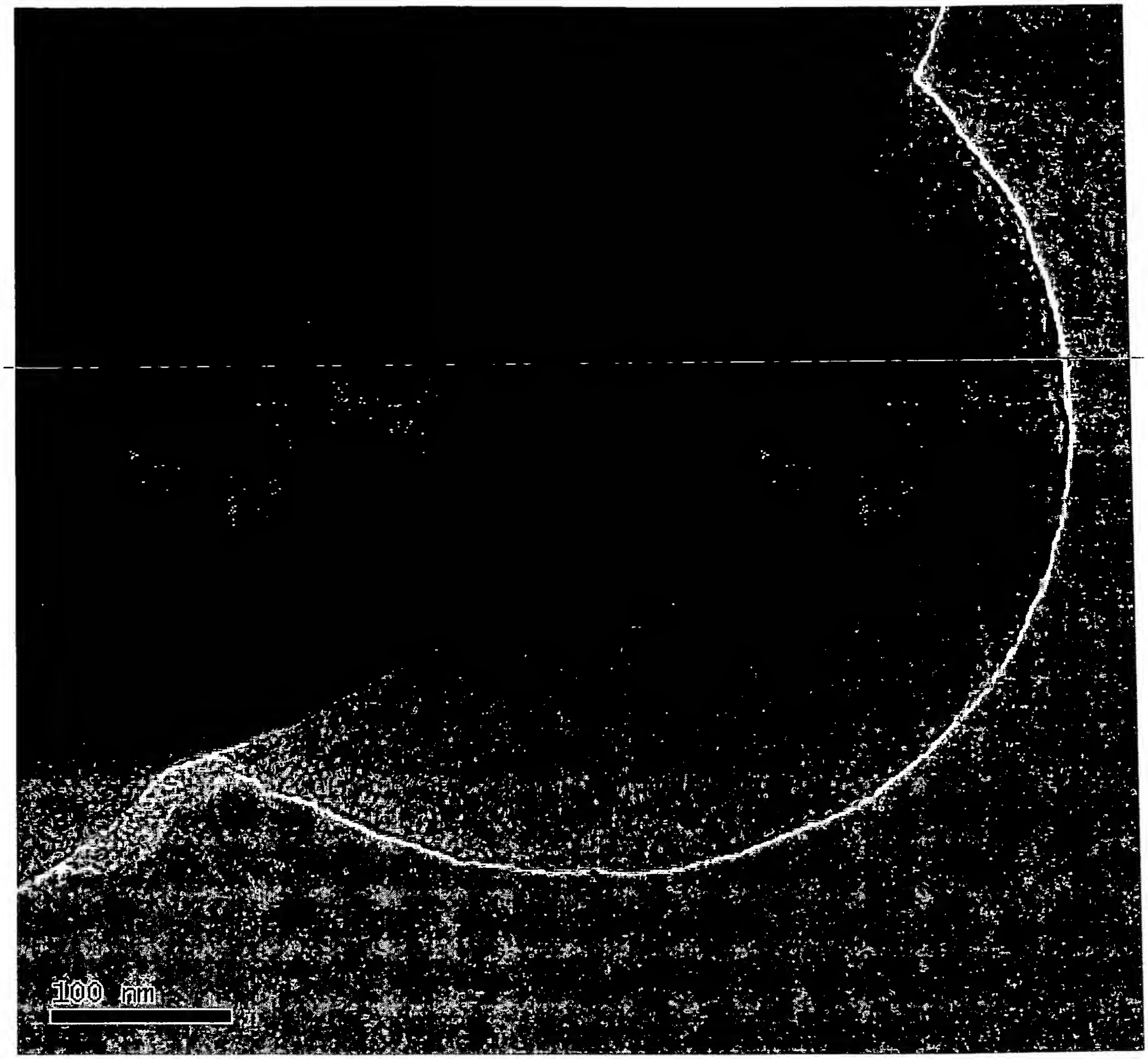


EXHIBIT 25

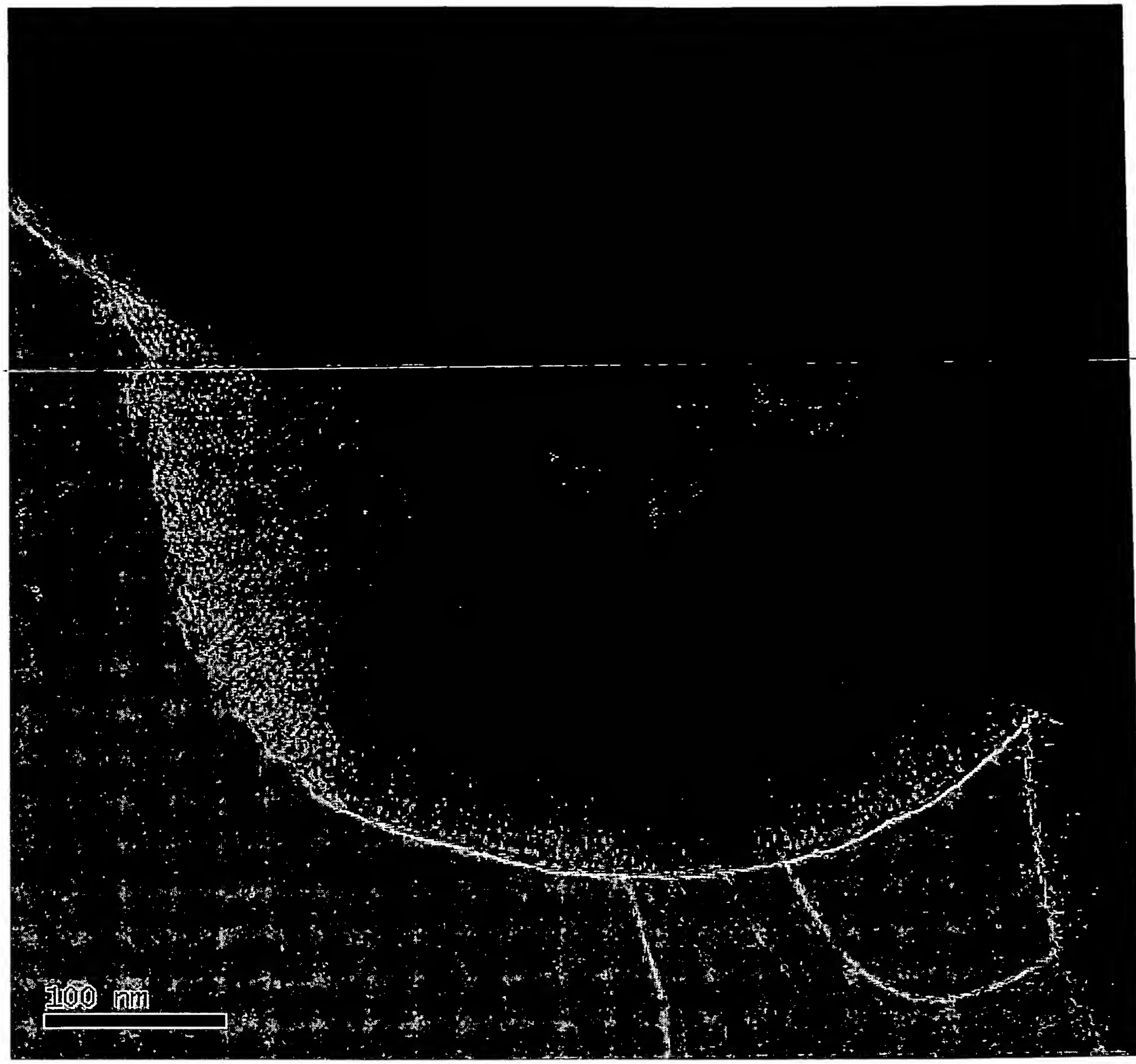
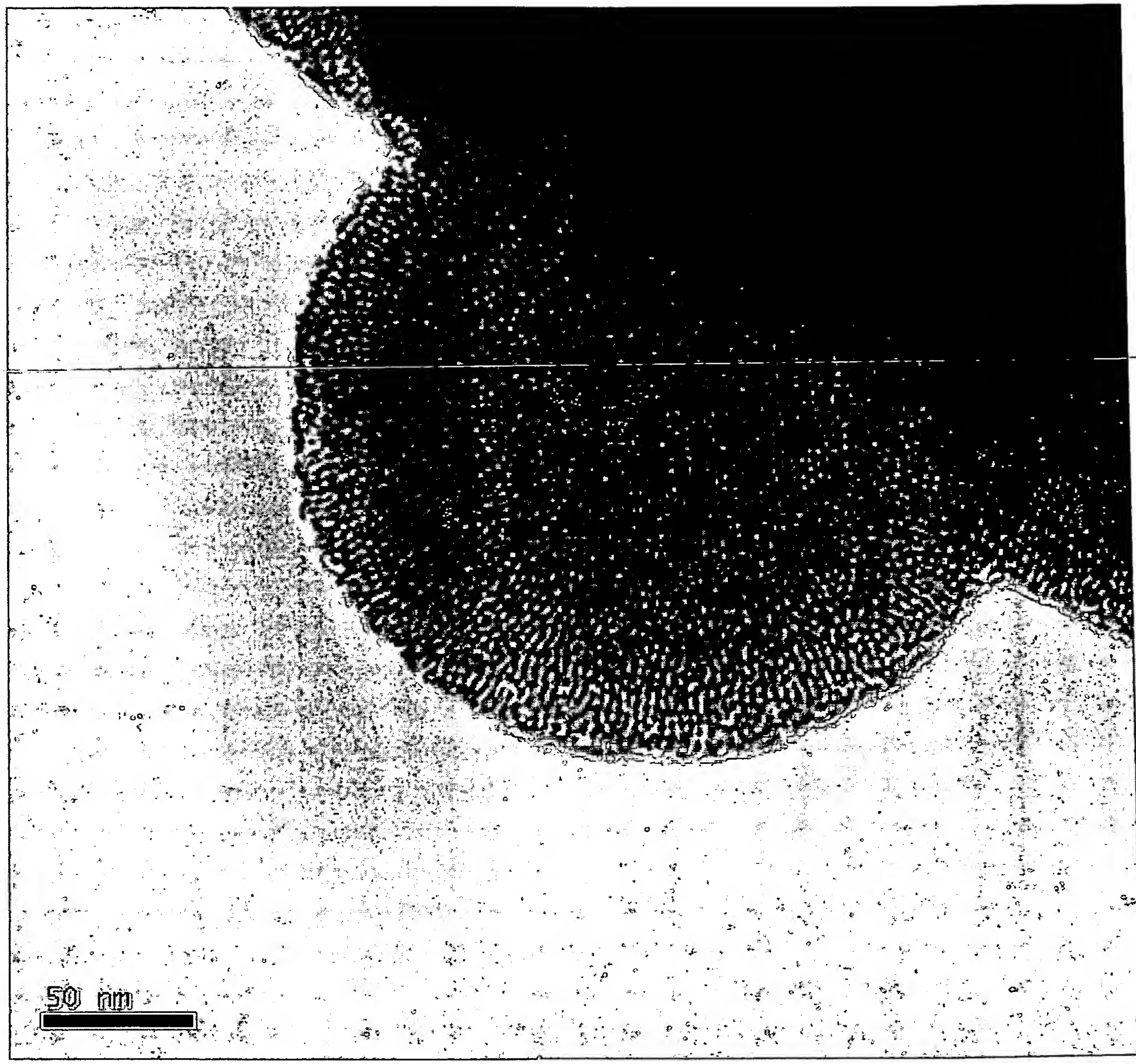


EXHIBIT 26



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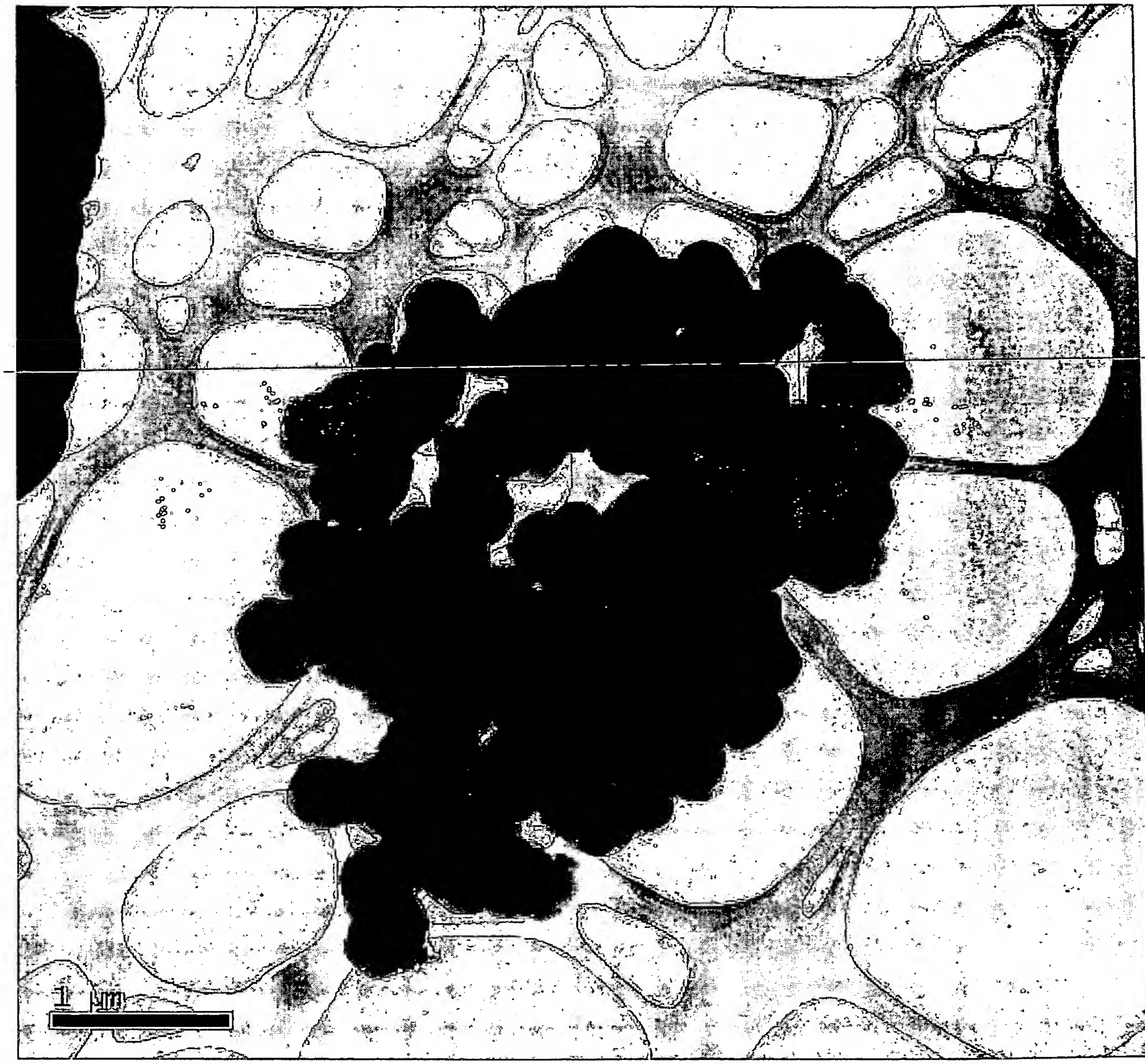

EXHIBIT 28